

## **Report for 2002AL4B: Treatment of Heavy Metal-Contaminated Runoff Using Straw Coated with Sulfide**

- Conference Proceedings:
  - Reters Robert W., S. Nunez, L.A. Blankinship, and J. Gauthier, 2003. "Stability of Straw Coated With Sulfide and Used for Treatment of Heavy Metal-Contaminated Runoff", in Conference Proceedings: Green Chemical Engineering Topical Conference, National AIChE Meeting, New Orleans, LA, pp. 139-151.

**Report Follows:**

# **“TREATMENT OF HEAVY METAL-CONTAMINATED RUNOFF USING STRAW COATED WITH SULFIDE”**

## **a. A statement of the problem and research objectives:**

Runoff from construction sites, roofs, and roadways is known to contain heavy metals as trace contaminants, and can effect the bioecosystems near these runoff sites. Urban stormwater runoff has been recognized as a substantial source of pollutants to receiving waters [Davis et al., 2001]. Urban settings are a focal point for environmental contamination due to emissions from industrial and municipal activities and the widespread use of motor vehicles [Callender and Rice, 2000]. During storm events, a considerable increase in the concentrations of particle number, suspended solids mass, organic carbon, iron, and zinc have been observed in runoff streams [Characklis and Wiesner, 1997]; the concentration of zinc in runoff was highly correlated with organic carbon and iron exists primarily in the macrocolloidal fraction. Hares and Ward [1999] studied the concentration of motorway-derived contaminants including V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Cd, Sb, and Pb, were measured in unfiltered stormwater collected during the initial stages of storm events. Higher levels of motor-derived heavy metal contamination exists in stormwater runoff from road sections with a higher average daily traffic density. The transport of anthropogenic constituents by runoff from urban roadways can adversely impact the quality of adjacent receiving waters and soils [Sansalone et al., 1996]. Heavy metal elements are the most persistent constituents found in pavement runoff [Sansalone et al., 1996]. Legret and Pagotto [1999] conducted a study investigating the quality of pavement runoff water from a 275-m motorway section over a one-year time frame, during which 50 rain events were sampled. Two different types of pollution were revealed; the first type was identified as chromic pollution and included suspended solids, chemical oxygen demand, total hydrocarbons, lead, and zinc. The second type of pollution was seasonal and incorporates chlorides, sulfates, suspended solids, and heavy metals due to the use of deicing salt in the wintertime. Runoff from roads have negative effects on biotic integrity in both terrestrial and aquatic ecosystems [Trombulak and Frissell, 2000]. Roads affect soil density, temperature, soil water content, light levels, dust, surface waters, patterns of runoff, and sedimentation, as well as adding heavy metals (especially lead), salts, organic molecules, ozone, and nutrients to roadside environments [Trombulak and Frissell, 2000]. The runoff chemistry from uncontrolled discharges of highway runoff can significantly impact receiving water quality and may require remediation by appropriate stormwater best management practices [Marsalek et al., 1997]. This project seeks to develop an efficient and low-cost technology to capture heavy metals from contaminated runoff, namely using straw that has been coated with sulfide compounds to bind the heavy metals to the straw.

## **The objectives for this research project are listed below:**

- To determine whether sulfide adsorbed on the surface of straw/hay will serve as an effective binding agent/precipitation agent for removal of heavy metals from solution (e.g., run-off from sites);
- To identify preliminary conditions (e.g., pH, sulfide dosage/unit weight of straw, etc.) whereby heavy metals are effectively removed from solution;
- To determine adsorptive capacities of the heavy metals on the straw; and
- To determine the break-through characteristics of the heavy metals through the pack-bed straw reactors.

## **b. A brief explanation of methodology:**

The scope of the research is three-fold: 1. Performing bench-scale batch isotherm characterization of the selected heavy metals onto straw and hay (both untreated and treated with sulfide compounds), 2. Performing continuous flow of heavy metal solutions through a packed-bed column containing straw, and 3. Modeling the bed depth-service time behavior of the heavy metal solutions through the columns to determine column breakthrough.

### c. Principal findings and significance:

Isotherm experiments were performed in which different dosages of straw were subjected to different concentrations of heavy metal solutions (containing iron, cadmium, chromium, and lead). Results from these experiments are summarized in Tables 1 and 2. The adsorption/uptake of heavy metals onto the straw were modeled using the Langmuir and Freundlich isotherms:

$$\text{Langmuir: } q_e = \frac{Q^0 b C}{1 + bC} \quad \text{Freundlich: } q_e = K_N C^{1/n}$$

Table 1. Summary of Isotherm Parameters for Heavy Metal Adsorption onto Straw (Straw Dosage = 1.0 gm/L); pH ~ 2.2

Isotherm Model	Parameter	Heavy Metal			
		Iron	Cadmium	Chromium	Lead
Langmuir	$Q^0$ , (mg/g)	3.979	0.305	-0.281	1.116
	$b$ , (L/mg)	0.234	0.587	-0.051	6.114
Freundlich	$K_N$	0.671	0.106	0.011	0.854
	$1/n$	0.567	0.4945	1.402	0.223

Table 2. Summary of Isotherm Parameters for Iron Adsorption Using Different Straw Dosages and Initial pH Levels.

Isotherm Model	Parameter	Dosage = 1.0 g/L		Dosage = 10.0 g/L
		pH ~ 2.6	pH ~ 4.05	pH ~ 4.1
Langmuir	$Q^0$ , (mg/g)	3.979	2.569	-5.244
	$b$ , (L/mg)	0.234	0.172	-0.028
Freundlich	$K_N$	0.671	0.374	0.1545
	$1/n$	0.567	0.561	1.081

Straw is an excellent medium for constructing a barrier to urban and industrial runoff. It is readily available and relatively inexpensive. Straw also has the potential for chemical modification to increase its ability to remove pollutants such as heavy metals from runoff. Being a plant material, straw is potentially biodegradable. The rate and extent of biodegradation influences its usefulness as a pollution barrier, especially if it chemical modified to improve its ability to remove heavy metals and other pollutants.

Plant material such as straw consists primarily of two fractions, the readily biodegradable portion and the slowly degradable portion. The readily degradable fraction consists of small molecules such as sugars, amino acids, and metabolic intermediates that are present in the plant cells. It also includes macromolecules such as proteins, carbohydrates, lipids, and nucleic acids. These components are easily and rapidly degraded by microorganisms unless they are entrapped in cell-wall bound cells and are not accessible to microorganisms. The slowly biodegradable fraction consists primarily of plant structural polymers such as cellulose and lignin. These structures are degraded by microorganisms, but degradation is a slow process.

In this study, the rate of biodegradation of straw was determined. Four straw preparations were investigated: untreated straw, straw treated with sulfide, straw treated with iron, and straw treated with sulfide plus iron. Each of these straw preparations were packed into columns (50 grams of straw) and treated with water on a daily basis. The column experiments were performed in triplicate. After 1, 2, 4, 8, and 16 weeks, the columns were dissembled and samples (10 grams) prepared for analysis by blending to a fine powder. Each sample was treated with neutral detergent to extract the readily degradable fraction. Total loss of straw from the columns was determined by comparing initial and final weight of the straw at various times.

**Total loss of straw.** On average, about 10-15% of the total weight of the straw was lost during the first few weeks. Although the initial rate of loss of rapid, after 8 weeks, the rate of straw loss from the columns was significantly reduced. By week 16, ~25% of the total weight of the straw was lost. The rate of loss of straw treated with different chemicals appears generally similar, with the most rapid loss occurring during the first week. The heterogeneity of straw clearly limits the sensitivity of measuring the

neutral detergent fraction. Consequently, trends beyond those described above cannot be determined with certainty. For example, it appears that the loss of straw was reversed in S4, the straw treated with sulfide + iron, but this is unlikely. An increase in the biodegradable fraction would occur if there were microbial growth on an exogenous substrate, but none was provided in this experiment. The conclusions from this part of the study are that ~10% of the total straw is rapidly lost from the columns during the first 2 to 4 weeks, and an additional 15% is slowly lost during the next 8 to 12 weeks.

**Biodegradability of the straw.** Initially, ~42% of the straw was readily biodegradable, based on neutral detergent solubility. About half of this material disappeared within the first couple of weeks, leaving ~20% of the straw as “readily biodegradable”. These results are consistent with the pattern of total loss of straw during this early period. The most rapid loss of the readily biodegradable fraction occurred during the first two weeks, regardless of the type of treatment (untreated, sulfide, iron, or sulfide+iron). The remaining readily biodegradable material is probably entrapped within cells by cell walls that contain cellulose, and are not accessible to microbial degradation until the cellulose is degraded. Following the phase of rapid removal of biodegradable material, there appears to be a slight increase in the biodegradable fraction when looking at the pattern for the average biodegradability of the straw. This may be due to the accumulation of microbial biomass that is growing on the slowly degradable fraction (cellulose and lignin). Visual and microscopic observations revealed the presence of bacteria and fungi during this phase. The slight increase in biomass, due to the increase numbers of microbial cells, is too small to be reflected in the total loss of straw measurements. From examination of patterns of degradation for different straw treatments (untreated, sulfide, iron, and sulfide+iron), it is concluded that ~50% of the readily biodegradable portion of the straw is degraded during the first few weeks of exposure to water in columns. The straw then remains relatively stable for the remainder of the test period. If sulfide is bound to the readily degradable fraction (e.g., proteins) or retained in cells that become susceptible to biodegradation during the first few weeks, it would be rapidly lost. However, if the biodegradable fraction were removed by incubation of the straw in water, reagents might bind to the more slowly degradable fraction and therefore be more stable and provide longer functionality.